PB84-215466

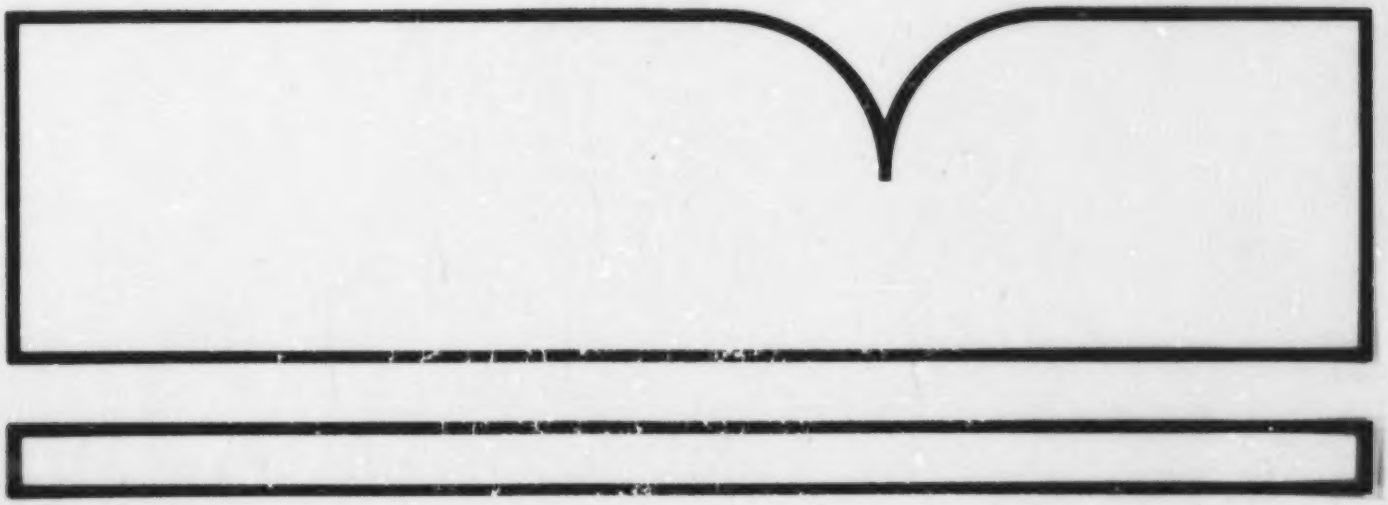
Evaluation of Alternate Methods for the Determination of VOC (Volatile Organic Compounds) Capture Efficiency at Surface Coating Operations

Radian Corp., Austin, TX

Prepared for

Industrial Environmental Research Lab.-Cincinnati, OH

Jul 84



U.S. Department of Commerce
National Technical Information Service
NTIS

PB84-215466

EPA-600/D-84-187
July 1984

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Darrell B. Hunt
Radian Corporation

John L. Randall
Radian Corporation

EPA Project Officer: Ronald J. Turner

Industrial Environmental Research Laboratory
U. S. Environmental Protection Agency
Cincinnati, OH 45268

INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OH 45268

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TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/D-84-187		PB84 215466

4. TITLE AND SUBTITLE	5. REPORT DATE
Evaluation of Alternate Methods for the Determination of VOC Capture Efficiency at Surface Coating Operations	July 1984
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Darrell B. Hunt, John L. Randall	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Radian Corp. 8501 Mo-Pac Blvd. Austin, TX 78766	C9HA1A
	11. CONTRACT/GRANT NO.
	68-03-3038, SBR-10
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
IERL-Ci, Office of Research & Development 26 W. St. Clair St. Cincinnati, OH 45268	Conference Paper
	14. SPONSORING AGENCY CODE
	EPA/600/12

15. SUPPLEMENTARY NOTES

16. ABSTRACT

Where solvent destruction systems are used to comply with EPA new source performance standards in the surface coatings industries, capture and control device efficiencies may have to be determined separately to demonstrate the combined overall reduction efficiency. The capture efficiency is determined as the percent of total VOC emissions that are captured and delivered to the control device. Presently, the EPA requires determination of capture efficiency through use of an exhausted enclosure around the operation and a gasphase material balance. The feasibilities of less costly and cumbersome alternate methods are examined. The alternate methods include material balances other than enclosure type gas-balances, use of tracers, computer modeling, and assumption/approximation techniques. The liquid/gas-phase measurement methodology using a total capture (100%) evaporation chamber. The pure solvent evaporation tests demonstrated that a combination of EPA Methods 2 and 25A for gas streams and a mass loss determination of liquid provided acceptable closure results (e.g., mean closure = 99.9% and coefficient of variation = 5.9%). The methodology was recommended for field evaluation.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Techniques to Measure Efficiency of VOC Capture Systems	Material balance, Capture efficiency, VOC's, Coatings	13B

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
Release	Unclassified	17
	20. SECURITY CLASS (This page)	22. PRICE
	Unclassified	

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

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Introduction

In recent years the U.S. Environmental Protection Agency (EPA) has developed a number of Federal regulations that limit emissions of volatile organic compounds (VOC) from new operations involving surface coating of web substrates. These include metal coil coating, publication rotogravure printing, and pressure sensitive tape and label coating.

The regulations restrict the amount of solvent that can be emitted per unit of coating solids used at the coater. Such a limit may be easily achieved and enforced if a suitable low solvent coating is available for use in the process. However, in many operations this is not the case. The plant must then install an abatement device that precludes the emissions by recovering or destroying the VOCs.

Determination of compliance when abatement devices are used, requires demonstration of emission reductions to the limits of the regulation. For operations employing solvent recovery type abatement devices, the emission reduction may be demonstrated by conducting a liquid-phase material balance (liquid recovered versus liquid used at the process). However, when solvent destruction type abatement devices are used, compliance determination is not easy unless the entire coating machine is enclosed and vented to the abatement device. Such total enclosures are being used by some manufacturers.

Other plants using solvent destruction devices prefer to use ventilated hood systems, which are obviously less than perfect, to capture some of the emissions and direct them to the abatement device. In these cases, determination of the reduction in emissions requires a knowledge of the fraction of total emissions actually captured by the system and sent to the abatement device (capture efficiency[1]), as well as the efficiency of the abatement device. There is no generally accepted method for measuring how well the capture system works (capture efficiency), consequently neither the plant operator nor the enforcement official can determine compliance.

To avoid such an impasse, the regulations promulgated to date allow the plant the alternative of erecting a temporary measurement enclosure. This enclosure must be a total enclosure around the process and must be drafted to a measurable fugitive vent stream. The fugitive stream and capture stream may both then be analyzed simultaneously for VOC mass flow. A comparison of the captured VOC mass flow rate with the total VOC emissions (captured plus fugitive) will provide a determination of capture efficiency.

The requirement of a performance test using a temporary total enclosure can be laborious and costly, but at the present time the EPA knows of no other way to verify compliance on these coating lines. If the temporary enclosure requirement serves as an incentive to install permanent total enclosures, then it may be a valuable contribution. If the temporary enclosure gains popularity as a short term measurement device and is removed, then it may become a source of aggrevation and cost to the plant.

To avoid the latter concern, the EPA initiated a study through Radian Corporation to evaluate the possibility of developing an alternate method for determination of capture efficiency. The study was conducted using a two-phase approach. The first phase was the identification and feasibility evaluation of potential alternatives in methodology. The second was the experimental testing of the method selected as the most feasible alternative. Both phases are discussed in the following sections.

Feasibility of Alternate Methods

Both direct and indirect capture efficiency measurement concepts were considered. Direct methods included material balance concepts. Indirect methods included the use of tracers, computer modeling, and other logical assumption concepts. Each is briefly described below.

Material Balance Concepts

Of the direct material balance concepts evaluated, the liquid/gas-phase concept was found to be the only logical alternative to a gas-phase material balance using an enclosure. The liquid/gas-phase material balance approach compares the gaseous VOC captured with the liquid VOC used at the process.

From a theoretical standpoint, the liquid/gas-phase material balance concept is very acceptable and feasible, with one exception. That is, where drying ovens are direct fired (which destroys a portion of the VOC content before the capture stream measurement point). In this case, a mass balance between liquid input and gas captured is technically infeasible. An advantage of the liquid/gas-phase balance is the ability to measure capture efficiency directly with no interferences in the normal flow of solvent vapors around the regulated process.

A review of liquid and gas-phase data from thirteen coating industry test sites provided only minimal support for the liquid/gas-phase approach. The majority of the tests were not specifically geared toward liquid/gas-phase material balances and the data collection techniques contained numerous shortcomings. These included inadequate characterization of the solvent and coating composition during test periods, non-continuous or intermittent measurement of liquid and gas streams, and short test periods involving non-steady state conditions. Several tests involving longer test periods and semi-steady state operating conditions yielded data which were considered to be representative of the capture efficiency.

Overall, it was concluded that the available test data were inadequate to either confirm or reject the liquid/gas-phase material balance method. It was further concluded that this approach requires careful characterization of liquid and gas stream compositions and flow-rates throughout test periods.

Tracer Concepts

Two separate tracer concepts were considered in this study. The first was a liquid tracer concept that simulates both the transition of the VOC from the liquid to gaseous form and the movement of the gaseous VOC mass to the capture and control system. The second was a gaseous or aerosol tracer

concept that simulates only the movement of the gaseous VOC mass to the capture and control system.

Liquid Tracers. The liquid tracer concept would require injection of a volatile liquid material which would possess vaporization properties similar to the solvent in use. A liquid/gas-phase material balance could then be conducted between the mass of liquid tracer injected and the mass of tracer measured in the gaseous form in the capture stream. The advantage of this approach would be the ability to distinguish the emissions of the test line from other adjacent sources in the area.

There is no indication of any previous application of the liquid tracer concept. Review of the potential application of this concept led to the conclusion that it is not economically feasible. This is primarily due to high costs expected to be associated with the custom compounding of the tracer materials and the cost of the analytical equipment required. Additionally, there would probably be reluctance from industry to inject any foreign substance into their coating compounds.

Gaseous Tracers. The gaseous or aerosol tracer concept would require the release of tracer material at each VOC vapor generation point on the regulated process and measurement of the tracer in the capture stream. A comparison between the mass of tracer in the capture stream and the mass released would yield the capture efficiency for each emission source segment. Alternately, the ratio of the tracer gas concentration measured in the capture stream under test conditions to the concentration measured under 100 percent capture conditions at the same release rate would yield capture efficiency for each emission segment. Either approach would also require a knowledge of the emission rate for each source segment in order to weight each segment's capture efficiency to the total for the process line.

In the gaseous or aerosol tracer concept, use of inert tracer gases was considered to be the only feasible approach. Aerosols tend to impinge on surfaces within the capture system, due to changes in the air flow direction, prior to reaching the measurement point. Inert tracer gases, such as sulfur hexafluoride, have been used extensively in other air movement assessments and offer many advantages, including low reactivity and easy detection at extremely low levels. An added advantage of sulfur hexafluoride is its high thermal stability making its use feasible in processes employing direct fired drying ovens.

The application of the gaseous tracer concept to VOC capture efficiency determinations is considered feasible but undeveloped. Before application may be possible, emission factors would have to be generated for the various emission segments of the total source, and the ability to release and measure the gas accurately must be demonstrated.

Computer Modeling

The modeling approach assumes the use of a code (model) that, when input with the required conditional data, will define the capture efficiency of VOC emissions under given emission control and site conditions through the use of a computer simulation. In order to represent capture efficiency as defined in this study and some NSPSs, codes are required to describe two separate activities which interact. These two activities are: (1) the formation of induced air flow patterns in and around the exhaust hoods and process line, and (2) the evolution and mobility of process VOC emissions.

A review of available literature and personal contacts identified no existing models specifically designed to meet the needs of this project. Most existing models addressing the mobility of airborne masses are related to activity in the outdoor ambient atmosphere and not the complex internal atmosphere of an industrial plant. No known models describing the movement of air in three dimensions around exhaust openings of varying geometry were identified. Additionally, industrial ventilation theory does not address capture efficiency as defined in this study. Therefore, new models would have to be developed to use this approach.

Because of the large number of affecting variables that would vary from operation to operation and plant to plant, the field task for gathering input data would be significant in order to apply the model. The amount of time required to collect input data would tend to reduce the intended efficiency of the model approach.

Based on the above information, the modeling concept is considered potentially feasible but not desirable because of the developmental requirements involved.

Assumption Concepts

Assumption concepts involve the use of logical assumptions and non-quantitative methods to conservatively approximate the capture efficiency. This concept makes use of visible chemical smoke to demonstrate capture and control of any emission source segment of the operation, which is not totally enclosed and exhausted to the control device. Source segments include coating feed tanks, coating applicator, web flashoff, and dryer.

In this approach smoke would be released at the surface of the emission source segment or released at any opening on a partial enclosure around a segment. If the smoke is visibly observed to be drawn entirely into the capture and control system, then the segment may be considered totally controlled. In the case where all emission source segments are visually demonstrated to be controlled, the capture efficiency may be assumed to be 100% or equivalent to a total enclosure.

In cases where total control is demonstrated only on certain source segments and not the entire operation, an "all or nothing" approach might be used, whereby only totally controlled segments are given credit as being captured. To obtain a quantitative capture efficiency value for the entire operation, the relative significance of each totally controlled emission source segment to the total operational emissions would have to be defined.

The use of these concepts was not reported in the literature. However, the use of smoke tubes in air movement studies is a common inexpensive practice. The application of the assumption concept appears fairly straightforward in the determination of total operation control and could be easily implemented where applicable.

In the second case, where only certain source segments are totally controlled, there would be a requirement to develop emission factors for each specific coating operation and source segment. The costs associated with the development of emission factors may not be warranted based on the conservative estimates of capture efficiency that would be derived.

Experimental Testing

Several test concepts or methods were considered feasible based on the evaluation described above. However, no single method was fully developed nor applicable to all possible test conditions and scenarios. Therefore, the direction of the study was not easily defined.

The liquid/gas-phase material balance method was chosen as the direction for the testing phase. This decision was based on the premise, that direct measurements are more readily accepted than indirect ones, that the material balance methods are generally further developed than the indirect methods, and that the liquid/gas-phase material balance methodology had not received sufficient testing in past efforts.

The experimental testing of the liquid/gas-phase material balance method was divided into two phases: (1) laboratory testing and (2) field testing. At the time of this publication, both phases have been completed; however, the field test data have not been analyzed. Therefore, only the laboratory testing results are reported at this time.

The laboratory testing was considered necessary because of the difficulties encountered in assessing the test methodologies and results from previous field tests. It was considered strategically important to begin testing under the simplest conditions and work up in complexity, and to be able to control and measure all streams for verification of test results. The laboratory approach met both of these criteria.

The purposes of the laboratory experimental work were to evaluate the ability to measure each required parameter accurately, compare alternate techniques for measuring specific parameters, and assess the overall ability to close liquid/gas-phase material balances under controlled conditions.

Approach

A liquid/gas-phase material balance requires the measurement and comparison of the liquid VOC mass used at the coating operation and the gaseous VOC mass captured from the operation and sent to the control device. The capture efficiency is then calculated as follows:

$$\text{Capture Efficiency (\%)} = \frac{\text{Mass of Captured VOC}}{\text{Mass of Liquid VOC Vaporized}} \times 100$$

The mass of liquid VOCs used during a material balance test period is determined by maintaining an inventory of the liquid coating usage and determining the VOC content of the coating. The liquid use is typically determined by weighing aliquots, metering streams, or depth- gauging tanks. The liquid input includes the addition of solvent for viscocity adjustment or wash solvents used during the test period. Measurement of the liquid VOC input in the field is often complicated by recirculating coating streams, multiple coaters on a single production line, lack of measurable streams in the coating area (e.g. the coating tank which feeds the coater is located in an area outside the test boundaries), and multiple coating lines (test and non-test) sharing the same coating tank.

During the time that the liquids are being processed, the flow rate and VOC concentration of the captured gas stream(s) are measured to determine the mass of captured VOC. The flow rate and concentration are monitored on a continuous or semicontinuous basis because of fluctuations that typically occur.

In order to effectively evaluate the performance of the methodology, most of the variables which would be experienced in the field were eliminated or strictly controlled during the laboratory testing. The test system was designed as a simple flow-through evaporation chamber, thus providing 100% capture and minimizing the number of measurement parameters. Therefore, a known-capture efficiency was established for comparison with the measured and calculated values, and sources of error in measurement were reduced to the lowest level.

The only field test variables that were incorporated into the laboratory experimental design were those that were easily simulated and controlled and that might directly affect the statistical evaluation of the methodology. The experimental design provided a range of measurement conditions that might exist at various plant test sites (e.g. varied compositions of organics, mass throughputs or run periods, and gas stream flow rates).

For practical purposes, the gas flow rate measurement methods were evaluated separately from the other measurement parameters and the mass balance closure tests.

Test Apparatus

To satisfy the previously stated objectives of the experimental work, the test apparatus was designed as a simplified evaporation chamber with the ability to control the airflow, the ability to contain all emissions in a measurable gas stream, provisions for incremental measurement of liquid mass flow, and adequate ports for gas sampling and flow rate determinations. The test apparatus is shown in Figure 1.

The air inlet, evaporation and mixing chambers were constructed separately of 1/4 inch plexiglass, each forming a rectangular duct. Each chamber was attached to the other with flexible sheeting in order to assure free movement of the evaporation chamber on the balance.

The evaporation chamber was designed with a removable top for easy access to the evaporation pan. An aluminum pan warmed by an electric heat tape was placed in the bottom of the chamber and used for evaporation of all liquids. The evaporation chamber was mounted on a laboratory balance for measurement of liquid mass. An angled plexiglass baffle was installed just prior to the evaporation chamber to deflect the air away from the evaporation pan and balance.

The mixing chamber was fitted with a vertical perforated plexiglass plate to create turbulent mixing conditions for the solvent vapor and air. The exit end of the chamber was a rectangular-to-round transition and was rigidly attached to the measuring duct.

To ensure the applicability of the EPA reference method criteria for gas flow rate measurements, the measuring duct was designed of a round, rigid pipe, 12 inches in diameter and 120 inches long. To provide the measurement points (optimum and non-ideal) for the velocity traverses, two

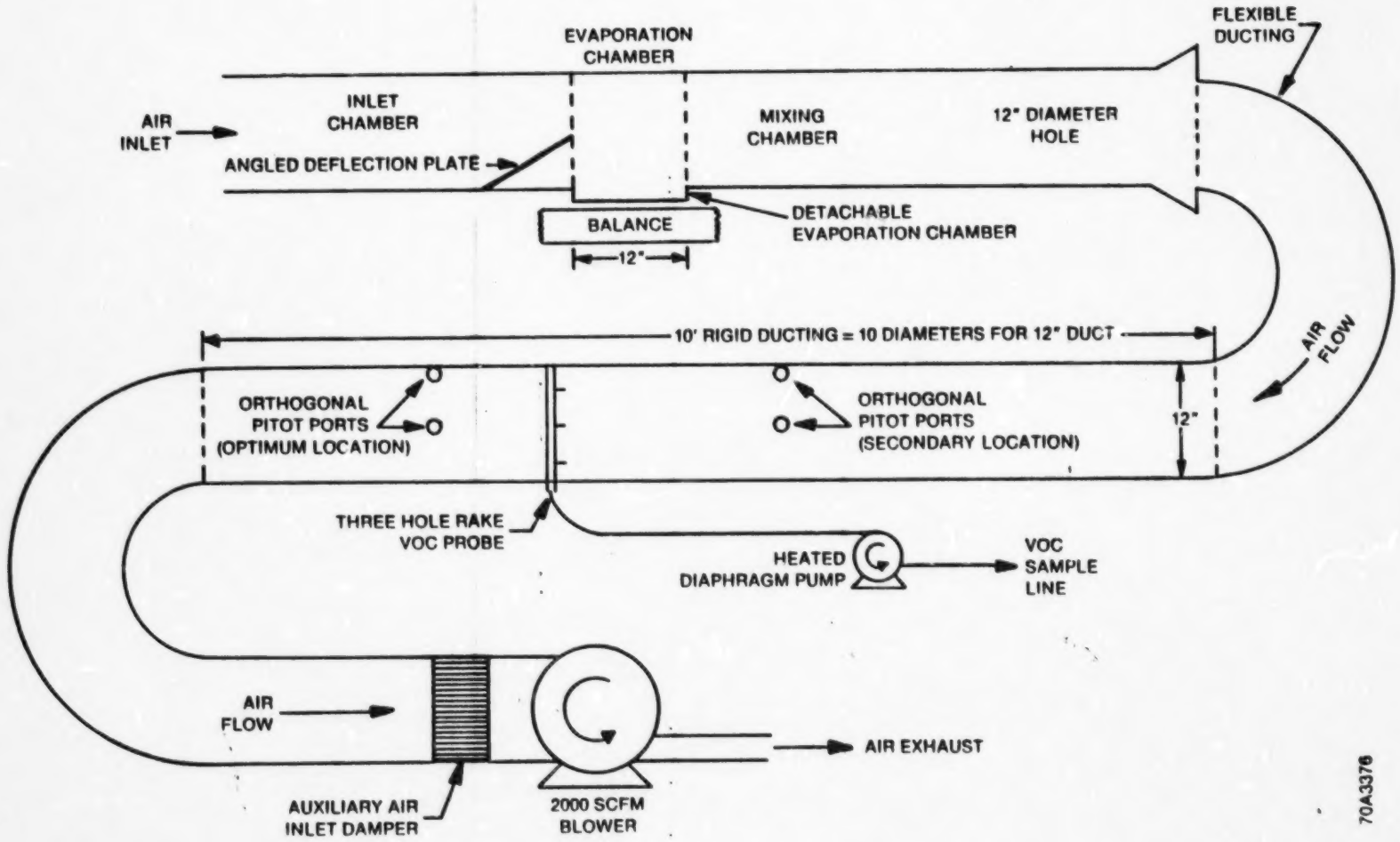

Figure 1. Test Apparatus for Laboratory Study of Capture Efficiency

orthogonal holes were drilled at two diameters from the exit end (optimum point) and two more at the midpoint in the length (non-ideal).

For collection of gas-phase samples to determine VOC concentrations, a piece of 1/4 inch stainless steel tubing with 1/16 inch holes centered at 2.0 inches, 6.0 inches, and 10.0 inches was installed at a 45° angle and 12 inches upstream of the ideal velocity measurement ports. A solvent laden air (SLA) sample line made of teflon was attached to the three-hole rake type probe and heated diaphragm pump and directed to the hydrocarbon analyzers.

Air flow through the system was induced by a nominal 2000 SCFM blower attached to the exit end of the system. Air from the measuring duct was directed to the blower inlet through approximately 20 feet of 12 inch rigid ducting. A series of damper holes were cut into this ductwork which could be covered or uncovered to regulate the air flow rate through the test apparatus.

Test Procedures and Methods

Gas Flow Rate Experiments. In the gas flow rate experiments, thirty-six sets of flow measurements were performed while varying the flow rate, measurement location, the pitot tube type, the differential pressure measuring device, and the personnel operating the instrument. Velocity traverses were conducted at both the optimum and non-ideal locations following the EPA method 2 criteria for the non-ideal location. During each series of velocity traverses other miscellaneous measurements were made, as required by Method 2, to determine the gas volumetric flow rate.

Test runs were conducted in groups based on set flow rates in order to maintain a common condition for evaluation of the other variables.

Mass Balance Experiments. In the mass balance experiments, twenty-four experimental runs were conducted using available liquid and gas measurement methods. The composition of organics, the mass throughput of organics, and the SLA flow rate were varied from one run to the next.

In these experiments, a known quantity of liquid solvent or coating was placed in the heated pan located in the evaporation chamber. Air was pulled through the system at discrete flow rates to produce a mass flow of SLA through the measuring duct. While the known quantity of liquid solvent was being evaporated, the resulting VOC concentration and the flow rate of the SLA stream were monitored. All of these measurements, including loss of liquid, were recorded at the same frequency to facilitate incremental determination of mass balance closure. Each experimental run was terminated when the VOC concentration in the SLA stream fell below the background level.

The gas-phase VOC concentrations were determined by three different analytical methods. The methods used were slight modifications of EPA Method 25A, EPA Draft Method 18, and NIOSH Method 127. The first method used flame ionization detection (FID) to provide total hydrocarbon (THC) concentrations. Similarly, the second method also used an FID for quantitation, but organic species in the sample were chromatographically separated prior to detection. The third method used charcoal tube adsorption of VOCs followed by solvent extraction and extract analysis by GC/FID.

EPA Method 25A and Draft Method 18 were utilized in each run of the experimental set, while NIOSH Method 127 samples were collected only on selected runs. The Method 25A measurements were made at one minute intervals. The Draft Method 18 measurements were conducted at seven minute intervals.

Method 25A specifies that THC determinations be performed using a continuous monitor equipped with an FID. Method 25A type monitoring on this project was performed on a semi-continuous basis using a Byron Model 401 THC analyzer (FID) in the THC mode.

Draft Method 18 type analyses were performed on the same sample gas stream delivered via the multiport manifold. The Method 18 instrumentation included an AID Model 511 GC with an FID.

NIOSH Method 127 type analyses deviated from the NIOSH method in that charcoal tubes were attached directly to the pressurized sample line rather than using a personal sampling pump. The flow through each charcoal tube was set and monitored by a Byron Model 90 mass flow meter/totalizer connected to the exhaust end of the tube. The charcoal tube analyses were performed by desorbing the front section of each tube with carbon disulfide and then injecting the sample into a Varian Series 1400 GC/FID.

Gas flow rates were measured midway through each run by EPA Method 2 without modification. An S-type pitot and inclined manometer were used to measure differential pressures through a complete traverse performed during each evaporation run. Additionally, the gas flowrate was monitored continuously during each run to assure no changes in flow.

Mass measurements of liquid VOC used were made on a calibrated laboratory balance. The balance was permanently placed under the evaporation chamber to monitor the weight of the chamber and any liquid that it contained. During each evaporation run, an initial weight of liquid was recorded. Periodically, at 5 or 10 minute intervals during the evaporation phase and at the end of each run instantaneous weights were recorded. The mass of solvent evaporated was determined by difference. Verification of the mass of each liquid charge to the evaporation chamber was performed by weighing the solvent storage bottle before and after applying its contents.

The vast majority of the laboratory tests involved pure solvents, i.e., no solids. However, in several test runs commercial coatings containing solids were used. For the laboratory tests, the solvent VOC weight loss was all that was required to perform a mass balance calculation. However, in the field where solids are transferred as well as VOC, the volatile content of the coating mixture will have to be determined, probably by EPA Method 24.

Results

Gas Flow Rate Results. The gas flow rate experiments were conducted according to a fractional factorial test matrix. The objective of the study was to evaluate the main and low order interaction effects associated with EPA Method 2 type flow rate determinations. Table 1 presents the variables studied, the level of each variable, and the results of the testing.

In the gas flow rate experiments, all test runs calling for a particular flow rate were conducted in sequence at the same setting with no change in the duct work or blower configuration. The velocity was set in the range of the specified level (e.g. 20, 30, or 40 feet per second) to

TABLE 1. Test Matrix and Results For Gas Flow Rate Experiments

Test No.	Pitot Tube Type[1]	Pressure Measurement Device[2]	Sampling Location[3]	Nominal Flow Rate (ft/sec)	Personnel[4]	Velocity Measurement (ft/sec)
1	S	Mag	NI	20	Chem	18.2
	Std	IM				18.3
2	S	Mag	OPT	30	Tech	31.4
	Std	IM				31.0
3	Std	Mag	OPT	30	Chem	32.0
	S	IM				30.5
4	S	Mag	NI	40	Chem	37.1
	Std	IM				38.8
5	Std	IM	OPT	40	Tech	40.1
	S	Mag				37.0
6	Std	Mag	OPT	20	Tech	18.9
	S	IM				17.3
7	S	IM	NI	20	Engr	18.8
	Std	Mag				19.6
8	S	Mag	NI	40	Engr	38.1
	Std	IM				39.3
9	Std	Mag	OPT	40	Engr	40.3
	S	IM				39.2
10	Std	Mag	OPT	20	Chem	19.2
	S	IM				18.4
11	S	IM	NI	40	Tech	39.2
	Std	Mag				39.6
12	S	Mag	NI	30	Engr	32.0
	Std	IM				31.5
13	S	Mag	NI	20	Tech	18.6
	Std	IM				18.3
14	Std	IM	OPT	20	Engr	20.0
	S	Mag				18.5
15	Std	Mag	OPT	40	Chem	39.7
	S	IM				40.9
16	S	IM	NI	30	Chem	30.8
	Std	Mag				31.4
17	S	Mag	NI	30	Chem	31.6
	Std	IM				30.7
18	Std	Mag	OPT	30	Engr	31.5
	S	IM				31.3

[1]Std = Standard Pitot. S = S-type pitot
[2]Mag = Magnehelic gauge. IM = inclined manometer
[3]OPT = Optimum location (2 diameters upstream/8 diameters downstream).
NI = Non-ideal location (5 diameters upstream and downstream).
[4]Chem = Chemist. Engr = Engineer. Tech = Technician.

produce data for a widely varied range of flow rates. Thus, the absolute values obtained for velocity are not as important as the relationship between grouped data for each velocity range setting.

Analysis of all velocity data sets indicated excellent precision with coefficients of variation not exceeding 4%. The greatest variability in the data was seen at the lowest flow rate, where minor discrepancies have a more pronounced effect.

Analysis of variance (ANOVA) techniques were used to test the statistical significance of first and second order effects from each of the variables (e.g. instrumentation used, location of measurement, operator). In only a few cases were any of the interaction effects considered statistically significant. The analysis indicated differences of marginal significance (α=.10) in the data obtained from different type pitot tubes at the lowest flow rate and from differences in pressure measuring devices at the middle flow rate (α=.05). The combination of S-type pitot tube and Magnehelic(R) Gauge was found to produce significantly different data (α =.01) from other combinations at the highest flow rate.

Overall, no single variable or combination of variables was considered to have any practical significance. However, it was considered advisable to avoid combining the S-type pitot and Magnehelic(R), particularly at higher flow rates.

Mass Balance Results. The mass balance experimental data were evaluated as three separate groups based on the VOC concentration measurement method (e.g. EPA Method 25A, EPA Method 18, and NIOSH Method 127). This provided a comparative evaluation of the three VOC measurement methods as well as the overall assessment of the ability to close the balance under variable conditions. Table 2 presents the test matrix and results. Additionally, a statistical analysis was made of each set of data similar to that in the gas flow rate analysis. The results of this analysis are given in Table 3.

Method 25A closures were by far the most successful in this set of experiments. Accuracy, bias, and precision were evaluated for the pure solvent and the commercial mixture experiments as separate groups. Accuracy seems more than adequate for each group since the mean closure values were, respectively, 99.9% (88.5-110%) and 102.2% (93.5-119). Bias for either group was not statistically significant, since 100% was included within the 95% confidence interval in both cases. Precision, or variability, estimates for the two groups were excellent, since the coefficients of variation were 5.9 and 8.9%, respectively. Test results for the commercial coatings test runs were less accurate than pure solvent runs, probably due to the smaller change in liquid mass and lower SLA concentrations.

The only variable found to have any statistical significance on the Method 25A data was the solvent amount. As a practical matter, this marginally significant effect would be difficult to explain since the mid-level (1.0 liter) results seem to deviate from the low and high level results. Thus, none of the variables nor combination of variables seem to have any great effect on the closure technique results.

Method 18 closure data were evaluated for accuracy, bias, and precision in the same manner as the Method 25A data. Based on mean closure values of 93.6 (73-264%) and 106.8% (86.2-186%) for the pure solvents and commercial mixture tests, respectively, the method appeared to be only marginally

Table 2. Mass Balance Closures

Elapsed Time[1] (min)	Solvent Type	Solvent Amount (liters)	Measured SLA Flow Rate[2] (SCFM)	Method 25A Closures[3] (%)	Method 18 Closures[4] (%)	NIOSH 127 Closures[4] (%)
100	MEK	2	832	100	73.0	397
56	Toluene	0.5	1400	101	98.0	210
140	Toluene	1	843	96.1	88.5	171
61	Mixture[5]	1	1417	108	94.3	127
86	MEK	2	1825	88.5	103	117
51	MEK	1	1471	107	88.5	NM[6]
53	Mixture[5]	0.5	1395	100	124	NM
150	Toluene	2	1406	99.0	119	NM
70	Mixture[5]	0.5	844	89.3	82.0	95.2
70	Mixture[5]	1	1753	110	264	NM
105	Mixture[5]	1	918	101	87.0	153
35	MEK	0.5	1718	100	76.9	45.2
81	Mixture[5]	2	1461	100	89.3	68.5
77	Toluene	1	1700	95.2	87.0	111
56	MEK	0.5	844	103	92.6	NM
49	Mixture[5]	0.5	1787	100	95.2	74.6
60	Mixture[5]	2	1771	102	73.0	172
175	Mixture[5]	2	859	95.2	82.0	385
50	MEK	1	1834	107	77.5	NM
156	Comm1[7]	1	1411	119	90.1	NM
190	Comm2[8]	1	1769	93.5	117	NM
121	Comm2[8]	1	922	99.0	86.2	118
120	Comm2[8]	1	1427	104	98.0	NM
241	Comm3[9]	1	1730	99.0	186	NM

[1]Elapsed time for each analysis varied due to cycle time and sensitivity difference

[2]Flow rate measured by EPA Method 2 during each run. (SCFM = 47.124 x ft./sec.)

[3]Calculated from (CW x 100/TW), where CW = sum of gaseous VOC masses from the VOC concentration and SLA flow rate, and TW = total weight loss of liquid.

[4]These data are the arithmetic average of the MEK and toluene closures.

[5]Mixture of 50% each by volume of MEK and toluene. Individual weights were used in the closure calculations.

[6]NM = not measured.

[7]Commercial mixture of rubber in MEK, specified by the manufacturer to contain 31% solids by weight.

[8]Mixture described in 7 above diluted approximately 10:1 with MEK.

[9]Mixture described in 7 above diluted approximately 2:1 with MEK.

Table 3. Statistical Analysis of Mass Balance Tests

Analysis Type	Data Type	Mean of Closures (%)	95% Confidence Interval (%-%)	Number of Observations	Standard Deviation (%)	Coefficient of Variation (%)
EPA Method 25A/Byron 401 THC Analysis	Pure solvent (overall)	99.9	97.1 - 102.7	19	5.9	5.9
	Commercial mix (overall)	102.2	89.6 - 114.9	5	9.1	8.9
EPA Method 18/GC-FID with Speciation	Pure solvent (overall)	93.6	83.1 - 104.2	19	21.9	23.5
	Commercial mix (overall)	106.8	71.1 - 142.6	5	28.8	26.9
NIOSH Method 127/Charcoal Tubes	Pure solvent (overall)	113.2	71.0 - 155.5	13	70.5	62.2

accurate. The wide 95% confidence intervals (83.1 to 104.2% and 71.1 to 142.6%) tended to discount bias as the primary problem. There was not sufficient evidence in the Method 18 closure results to indicate significant main or interaction effects, at least to the 0.10 level. However, the variability estimates as measured by the coefficient of variation indicated that the particular methodology or instrumentation used was not adequate for measuring VOC capture efficiency.

Two possible explanations were postulated regarding the wide ranging Method 18 data. First, detailed review of the THC concentrations for each run showed variations with substantial up and down swings. The 7-minute interval data obtained by the Method 18 analyzer very likely missed a number of the peaks and/or valleys. Second, during some of the runs, it was apparent that the sensitivity of the Method 18 analyzer changed during the run. At one point, the analyzer's detector jet was mechanically cleaned and the sensitivity rose dramatically. The extent of this problem was not quantified.

Full statistical analysis was not performed on the charcoal tube data. However, the data indicate that the method is not adequate for performance testing. The most serious problem associated with this method seems to be its variability. As measured by the coefficient of variation, this was 62.2%. The variability could not be explained based on the available data.

Conclusions

Of the alternate methods considered for determining capture efficiency, the liquid/gas-phase material balance concept was determined to be the most feasible based on economics, technological development, and the applicability of the data that would be developed. The gaseous tracer concept and the assumed efficiency concept are also believed feasible but require a much greater degree of development.

Laboratory testing of the liquid/gas-phase material balance methods concluded that reasonable closure results and capture efficiency determinations can be obtained under controlled flow conditions. Gas flow rates determined by EPA Method 2 are not significantly impacted by the instruments used or the operator, and they are suitable for use in liquid/gas material balance type capture efficiency determinations. EPA Method 25A was found to be the most suitable method for measuring gaseous VOC concentrations of the three examined.